Defense Technical Information Center Compilation Part Notice

ADP023776

TITLE: Molecular Dynamics Study of Alkanethiolate Self-Assembled Monolayer Coated Gold Nanoparticle

DISTRIBUTION: Approved for public release, distribution unlimited

This paper is part of the following report:

TITLE: Proceedings of the HPCMP Users Group Conference 2007. High Performance Computing Modernization Program: A Bridge to Future Defense held 18-21 June 2007 in Pittsburgh, Pennsylvania

To order the complete compilation report, use: ADA488707

The component part is provided here to allow users access to individually authored sections of proceedings, annals, symposia, etc. However, the component should be considered within the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:
ADP023728 thru ADP023803

Molecular Dynamics Study of Alkanethiolate Self-Assembled Monolayer Coated Gold Nanoparticle

Brian J. Henz
US Army Research Laboratory (ARL),
Aberdeen Proving Ground, MD
brian.j.henz@us.army.mil

Michael R. Zachairah
Department of Mechanical Engineering and the
Department of Chemistry and Biochemistry, U. of
Maryland, College Park, MD and the National Institute
of Standards and Technology, Gaithersburg, MD
mrz@umd.edu

Abstract

Through molecular simulations we have observed that the surface of gold nanoparticles become highly corrugated by the adsorption of alkanethiolate self-assembled monolayers (SAMs). Furthermore, as the temperature is increased, the SAMs dissolve into the gold nanoparticle, creating a liquid mixture at temperatures much lower than the melting temperature of the gold nanoparticle. By analyzing the mechanical and chemical properties of gold nanoparticles at temperatures below the melting point of gold, with different SAM chain lengths and surface coverage properties, we have determined that the system is metastable. The model and computational results that provide support for this hypothesis are presented in this paper.

1. Introduction and Background

Nanoparticles are often used in applications where a high surface area to volume ratio is desired. Some of the typical applications include catalysis, biosensors, and use as drug delivery vehicles[1,2]. A major limitation of the expanded use of these nanoparticles is that the fabrication of nanoparticles with the desired morphology and structure is challenging[3–5]. Gold is a commonly used material for nanoparticle fabrication because of its resistance to oxidation and its interesting electrical, magnetic, optical, and physical properties. Furthermore there is a considerable knowledge base on functionalizing gold surfaces that are being ported to analogous particles. The results of these past efforts are built upon in this work in order to analyze more complex, and larger gold nanoparticle systems.

Coating of gold surfaces and nanoparticles with a self-assembled monolayer (SAM) creates many additional applications including lithography, lubrication, catalysis, biocompatible materials, and biosensors. There have been numerous experimental[6–8] and numerical studies[9] performed that have attempted to characterize the properties of alkanethiolate SAM coated gold surfaces. Simulations investigating alkanethiolate SAM coated gold surfaces accurately predict the c(4×2) superlattice structure of alkanethiols on an Au(111) surface. Additional work has predicted the segregation of SAM chains adsorbed on a gold surface by length, surface frictional forces, and phase behavior[10]. Efforts to characterize the alkanethiolate SAM coated gold nanoparticle system have been limited to atomistic simulations considering a single alkanethiol chain, and a small (less than 100 atom) gold cluster[11] or MD simulations of small nanoparticles that ignore gold-gold interactions[9,12].

The work in this paper is focused on understanding the effect of the alkanethiolate SAM on gold nanoparticles using MD simulations. Using the pair correlation function we estimate the melting temperature of the particle, and the affect that the SAM has on the particle surface. We clarify the relationship between surface coverage and structure of the particle by introducing a corrugation factor, and identify the phase transition mechanism of SAM coated gold nanoparticles. We find that the SAM coated particles are mechanically unstable as determined by the radial pressure profile.

2. Simulating the SAM Coated Gold Nanoparticle

In this effort the gold substrate atoms are explicitly considered as dynamic atoms, requiring that an accurate potential be used to simulate the atomic interactions. The embedded atom method[13–15] (EAM) and the effective medium[16–18] (EM) potentials have received the most attention for accurately simulating atomic gold
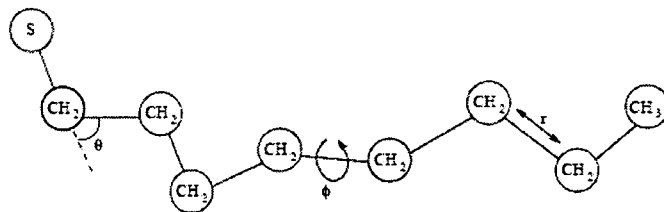
interactions and the interactions of other fcc lattice metals. We chose the EAM for modeling the gold substrate because of its reported accuracy, and the potentially useful extensions developed for the EAM for modeling surfaces, such as the extended EAM[19] (XEAM), and the surface EAM (SEAM).[20] The actual EAM potential used in this work is taken from the LAMMPS[21], 3 June 2005, software distribution. A detailed discussion of the method as used in this work can be found in Daw, et al.[13,14]

Recent efforts to simulate the elongation of a gold nanowire suggest that the second-moment approximation of the tight-binding scheme (TB-SMA) potential produces results that more closely approximates the experimentally observed results and the results from quantum computations.[15] In the aforementioned work, the authors compared various MD potentials including the EAM potential and quantum calculations to experimental results for the mechanical elongation of a gold nanowire. The finding is that the EAM potential predicts greater ductility and temperature affects than observed in the quantum simulations. The predicted affect of using the TB-SMA potential in this effort would be a less ductile gold nanoparticle resulting in slightly less surface corrugation. We also would expect to see a more negative internal pressure because the nanoparticle surface would be less accommodative to a tensile surface stress.

2.1. Modeling the Alkanethiolate Chain

The alkanethiolate polymer chain may be simulated with a range of computational complexity depending upon the resources available, and the accuracy of results required. For the simulations in this work we have chosen the united atom method (UA). In the UA method used here, each monomer is modeled as a single particle, e.g., S, CH_2, and CH_3 are the particles that make up the alkanethiolate polymer SAM.

The modeling of the alkanethiol chain using the united atom model is consistent with many of the published studies for the alkanethiolate coated gold nanoparticle system[10]. An example of the alkanethiolate polymer chain model used in this work is shown in Figure 1. The potentials used in the united atom model include a bending potential for the S-C-C bond and the C-C-C bond. There is also a dihedral potential for the X-C-C-X bonds, where X can be either S or C. The bond lengths along the chain can be held constant with the RATTLE[22] algorithm or they can be modeled as harmonic bonds as used here. Using a harmonic bond to describe the C-C and S-C backbone bonds allows the distance between the backbone atoms to change while not allowing the bonds to break during the simulation.

Figure 1. Sample alkanethiolate chain with 8 carbon atoms along the backbone

The potentials and parameter values for the bending angle and dihedral angle from Figure 1 and used in this work are given in Shevade, et al.[23], the bond stretch parameters are given in Rai, et al.[24]

2.2. Binding of Sulfur to Gold

The binding potential used to model the binding of the head sulfur atom of an alkanethiol chain to the gold substrate is of great interest as it affects the location, orientation, movement, and desorption of chains from the gold surface[25,26]. There have been many efforts, using *ab-initio* methods, devoted to finding accurate potentials for predicting the sulfur to gold binding potential for use in MD simulations. Since the Morse potential, Eq. (1), mimics a partially covalent bond, it is used in these MD simulations along with the parameters given by Zhang, et al[27] to model the sulfur-gold bond. The parameters for Eq. (1) are $D_e = 13.3$ kJ/mol, $\alpha = 1.38$, and $r_0 = 2.903$ Å.

$$U_{Morse}(r) = D_e \left[e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)} \right] \quad (1)$$

The binding energy of the alkanethiol to the gold surface has been determined to be around 184.1 kJ/mol, when all of the sulfur-gold interactions have been accounted for. Although this reported value is often referenced, there are numerous researchers that have reported the sulfur-gold bond energy to be 126.0 kJ/mol.[28,29], in which case the Morse potential parameter is $D_e = 9.108$ kJ/mol. This discrepancy in the binding energy is large, and so in this work we will investigate using both binding energies in order to understand the affect that binding energy has on the computed results.

3. Simulation Results

In this section, the results from the MD simulations are presented and analyzed. In order to study the affects of the alkanethiolate SAM on the gold nanoparticle we have computed many system properties including diffusion coefficients, radial pressure and density distributions, melting temperature, and the pair correlation function. A corrugation factor that describes the depth to which the gold surface is modified by the adsorbed

alkanethiol chains is also defined in this section. Each of these results is a data point of the changes the nanoparticle experiences with the adsorption of the alkanethiolate SAM.

Additionally, we will discuss the affect of various model parameters on the computed results. The most important of these parameters are the sulfur-gold binding energy and the gold-gold interaction potential.

3.1. Pair Correlation Function

The results of the pair correlation function gives insight into the structure of the material including whether the material is crystalline or amorphous. The pair correlation function for a bare 50Å diameter gold nanoparticle is presented in Figure 2 for a range of temperatures.
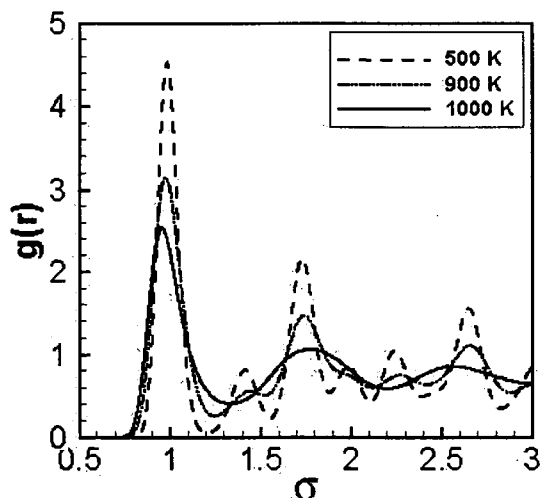

Figure 2. Pair correlation function for bare 50Å gold nanoparticle

The results in Figure 2 indicate that a phase transition occurs in the nanoparticle from a crystalline solid at 900K to a liquid at 1,000K and as expected, this range is below that of the bulk melting temperature of 1,340K[30].

In this section we compare the pair correlation function results for the uncoated gold nanoparticle to the results for an alkanethiolate coated gold nanoparticle. A complete surface coating is defined as one chain per 15.4Å^2 of surface area on the gold nanoparticle[31], and is about 30% denser than the packing density on a flat surface (21.4Å^2). The pair correlation function results for the alkenthiolate SAM-coated gold nanoparticle show a nanoparticle with a crystalline structure for temperatures below 400K and an amorphous structure above 600K. The pair correlation function is computed for the gold atoms only. By only considering the gold atoms in computing the pair correlation results, the structure of the

nanoparticle is analyzed separately from the SAM. The observed change in the pair correlation function results for the gold atoms indicates that a phase change occurs in the gold nanoparticle around 500K. Hence the melting temperature of the gold nanoparticle is lowered by about 500K from the adsorption of the alkanethiolate SAM.

In other simulations that use the lower sulfur-gold binding energy of 126 kJ/mol we have observed that at 500K the nanoparticle is still crystalline and undergoes a phase change at a higher temperature than when the 184 kJ/mol binding energy is used. Prior to the phase change some desorbtion of the alkanethiol SAM is also observed.
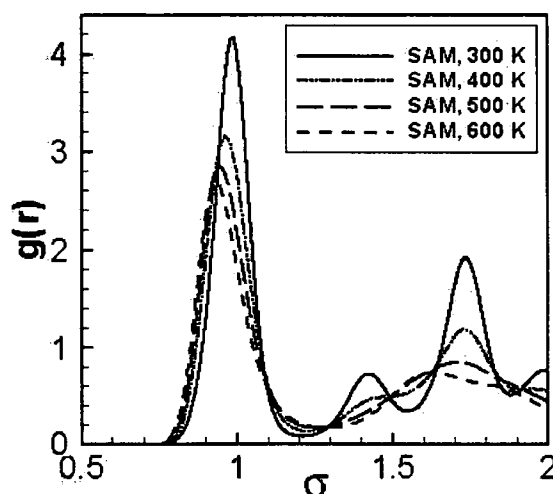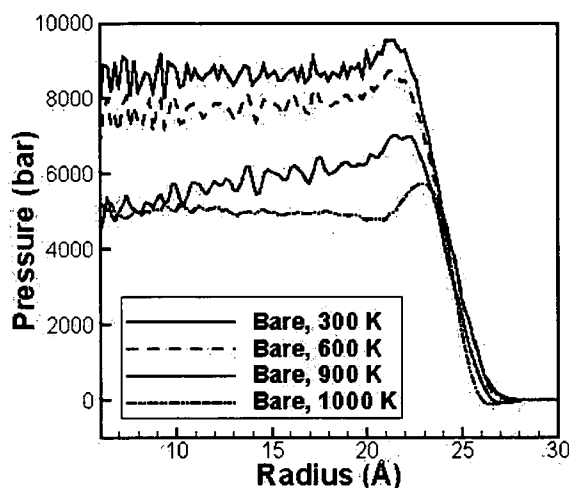

Figure 3. Pair correlation function results for the SAM coated 5Å gold nanoparticle

3.2. Radial Pressure Distribution

The radial pressure distribution is used in this work to quantify the affect of the adsorbed alkanethiolate SAM on the gold nanoparticle. In very small droplets the internal pressure can be much larger than the surrounding environment. For a droplet, or nanoparticle, internal pressure is computed in MD simulations as a radial pressure distribution. One method of evaluating the radial pressure distribution is to use the normal component of the Irving-Kirkwood (IK) pressure tensor.[32] The normal pressure at the surface of a nanoparticle or droplet is typically positive, indicating a compressive surface tension. The radial pressure distribution for an uncoated 50Å gold nanoparticle as a function of temperature is plotted in Figure 4.

Figure 4. Radial pressure distribution for 50Å gold nanoparticle at various temperatures.

In Figure 4 the "Bare, 1,000K" curve is for liquid gold and the other curves are for a solid gold nanoparticle. As the temperature of the nanoparticle increases, the surface pressure decreases. This decrease of pressure with increasing temperature is expected because the reported experimental surface tension data decreases with increasing temperature. From a dimensional analysis of the Young-Laplace theorem[33] shown in Eq. (2), this expected result is confirmed.
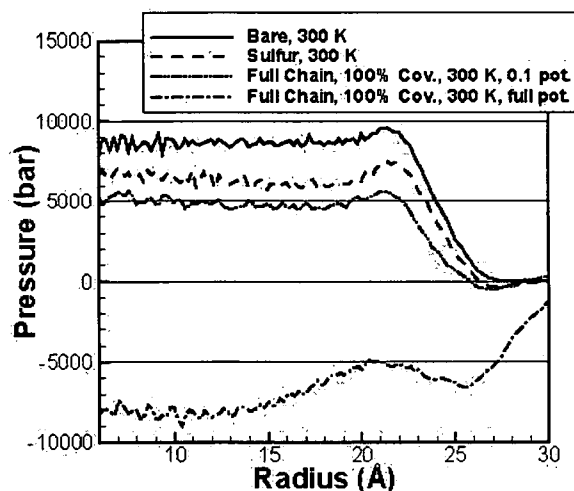
$$\Delta P = \frac{2\gamma}{r} \qquad (2)$$

In Eq. (2), r is the radius of the gold nanoparticle and ΔP is the difference in pressure between the interior and exterior of the droplet, i.e., $P_{inside} - P_{outside}$. Experimentally determined and published values for gold surface tension are wide ranging and available from a limited number of sources. For the liquid-gas interface, γ_{lg} is $1128 mJ \cdot m^{[33]}$. For a liquid-vacuum interface, γ_{lv} is about $1128 mJ \cdot m^{-2}$ at the melting point of gold[34]. It could be expected that the difference in measured surface tension between the liquid-gas and liquid-vacuum would be minimal. From the two published sources this is not the case and so for comparison purposes, we must consider these values as representative of the expected value. Evaluation of Eq. (2) for our 25Å radius particle and the published surface tension data for a vacuum interface results in a predicted internal pressure of about 6,000bar. This analytic result is close to that obtained from the MD simulation at 1,000K shown in Figure 4. With the wide range of available data for comparison, it can only be said that the predicted surface pressure and the simulated pressure are in reasonable agreement.

The combination of the results from the Young-Laplace and Rowlinson-Widom equations shows that the internal pressure computations for the uncoated gold

nanoparticle are reasonable and in the range expected. Unfortunately, there is no data available for comparison when considering the alkanethiolate coated gold nanoparticle surface.

From past efforts[35] it is expected that a surface coating will modify the nanoparticle internal pressure, by changing the surface tension, of the gold nanoparticle. This possibility is considered here by comparing the radial pressure distribution for gold nanoparticles with varying degrees of surface coatings. The systems considered include a bare gold nanoparticle, a gold nanoparticle with only sulfur atoms adsorbed onto the surface, and finally a gold nanoparticle with alkanethiolate chains adsorbed on the surface, but with varying interaction potentials. For bare and coated gold nanoparticles with weak SAM chain-chain interactions the internal pressure is positive, meaning a positive (compressive) surface tension. As observed in Figure 5, the pressure trends lower, and becomes negative on the interior of the fully coated nanoparticle as the chain-chain and chain-gold interaction potential parameter values are increased to the published values, indicated by "Full Chain, 100% Cov., 300K, full pot."

Figure 5. Radial pressure distribution for 50Å gold nanoparticle with alkanethiolate SAMs with differing interaction coefficients

As a first interpretation of this negative pressure result, one could consider the volume integral of the internal pressure distribution. Since the volume integral of the pressure distribution is negative, it indicates a mechanically unstable system, or a nanoparticle under tension. As seen in Figure 5, the negative pressure is observed in the interior of the nanoparticle, and only when full chain-chain and chain-gold interactions are considered. This negative pressure result indicates that the gold nanoparticle is experiencing a tensile stress and will change its configuration over time or with increases

in temperature in order to accommodate the positive stress or negative pressure. The chain-chain interactions apparently have a strong influence on the surface tension, and therefore the internal pressure of the nanoparticle. The strength of the interaction potential that will flip the internal pressure from positive and mechanically stable, to negative and mechanically unstable is still under investigation but is between 10% and 100% of the published potentials used for the alkanethiolate SAM interaction potential. Other factors that may affect the surface tension are the surface area per adsorbed alkanethiol chain, and temperature. Current efforts also indicate that modifying the sulfur-gold binding energy alone has little affect on the computed internal pressure. This indicates that the sulfur-gold binding energy has little affect on the internal pressure profile, and the results in Figure 5 are primarily due to the change in chain-chain interactions.

A negative surface tension resulting in a tensile stress inside a solid nanoparticle will exist for a time before creep[36] or an increase in temperature will lower the yield strength allowing the nanoparticle to yield and flow. For these reasons, the solid gold nanoparticle with an alkanethiolate coating is meta-stable at low temperatures, but will stabilize at higher temperatures by changing shape. In this particular case, we observed as discussed in the section on diffusion that the alkylthiol chains dissolve into the particle. This result has not been previously observed in simulations because the gold nanoparticle was assumed to maintain its shape, with the interaction of the alkanethiolate SAM constrained to the surface.
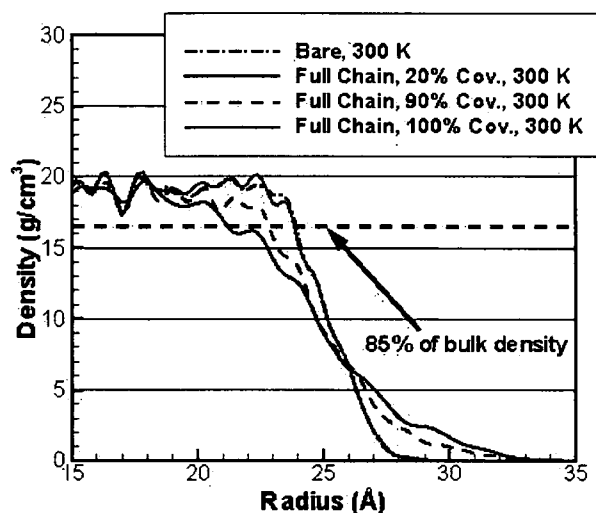
When using the lower sulfur-gold binding energy of 126.0 kJ/mol some alkanethiol chains are observed to desorb from the nanoparticle surface. As the desorption process proceeds, fewer alkanethiol chains are adsorbed to the surface and the internal pressure increases.

3.3. Radial Density Distribution

Thus far, the computed results show that the 50Å uncoated gold nanoparticle has a melting temperature between 900K and 1,000K (pair correlation function), the SAM chains are mobile on the gold surface (diffusion coefficient), and that there are two phases for the alkanethiolate SAM between 100K and 800K. In this section the radial density results are analyzed.

For bare nanoparticles, the radial density distribution for the gold atoms will change abruptly at the nanoparticle surface from the core density to zero. On the other hand, for coated nanoparticles, if the surface atoms move due to the presence of the alkanethiolate chains penetrating into the particle, the slope of the radial density distribution will be less steep. This phenomenon of the SAM chains penetrating into the nanoparticle surface is not a previously predicted result because past work

simulating alkanethiolate coated gold nanoparticles has assumed that the gold atoms do not move as a result of the interactions with the SAM. When analyzing the radial density, shown in Figure 6, it is apparent that the atoms near the surface of the gold nanoparticle are less densely packed than those in the nanoparticle core. This decrease in gold atomic density suggests that near the nanoparticle surface, the gold atoms are mixing with the alkanethiolate molecules.

Figure 6. Radial density of gold in alkanethiolate SAM coated gold nanoparticle for various surface coverage amounts

The results in Figure 6 show the expectedly steep slope for the radial density distribution of the uncoated gold nanoparticle. The slope decreases monotonically as more SAM chains are adsorbed onto the gold surface. This decrease in slope indicates that the atoms near the surface are more diffuse, resulting in the lower measured density of gold. The depth to which the gold core is affected we have labeled as the surface corrugation.

In order to quantify the surface corrugation we have defined by Eq. (3) a corrugation factor, C.

$$C = \frac{r(\rho = 0.85\rho_{bu})_{ba} - r(\rho = 0.85\rho_{bu})_{co}}{r(\rho = 0.85\rho_{bu})_{ba}} \quad (3)$$

where $r(\rho = 0.85\rho_{bu})$ is the radius where the computed gold density is 85% of the density of bulk gold, and the subscripts ba and co refer to the bare and alkanethiolate SAM coated gold nanoparticle, respectively. This definition of the corrugation factor will result in a value of 0.0 for the bare gold nanoparticle and maximum of 1.0 for a gold nanoparticle with impurities or a dissolved solute. For coated gold nanoparticles with various percentages of surface coverage the corrugation factor has been computed, and is listed in Table 1.

Table 1. Computed corrugation factors for alkanethiolate SAM coated gold nanoparticles

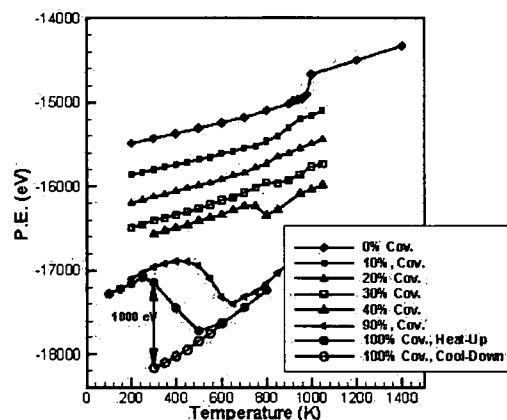| Coverage	$C_{184 \, kJ/mol}$	$C_{126 \, kJ/mol}$
Bare	0.000	0.000
10%	0.004	0.003
20%	0.004	N/A
70%	0.012	0.018
80%	0.018	0.013
90%	0.043	0.020
100%	0.107	0.081

The results presented in Table 1 show that the corrugation factor remains small, indicating little change in the nanoparticle surface, for SAM coverage below 90%. Once the coverage reaches 90%, the corrugation factor increases 2.5 times over the value at 80%, and increases by another factor of 2.5 times between 90% and 100%. With a corrugation value of 0.107 at full surface coverage, the core of the gold nanoparticle is only about 89% of its original size. This result has two implications; first, that the surface area of the gold nanoparticle has increased because the surface is no longer smooth but wrinkled, second, the SAM chains are able to form more bonds to the increased number of exposed gold atoms, potentially increasing the binding energy of the SAM to the gold nanoparticle. The results in Table 1 indicate an exponential dependence of the corrugation factor on the amount of surface coverage. For the lower (126 kJ/mol) sulfur-gold binding energy, the surface corrugation is lower for the 100% surface coverage simulation and indicates that the binding energy directly affects the nanoparticle surface corrugation.

3.4. Phase Behavior and SAM Solubility

The computed potential energy (PE) of the alkanethiolate SAM coated gold nanoparticle system is used to determine the critical temperature at which mixing and phase change will occur. The computed slope of the PE versus temperature curve from the MD simulation results are used to determine the heat capacity of the system.
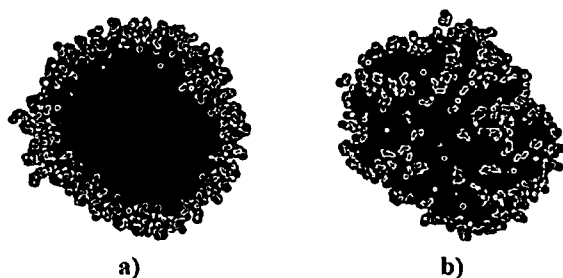
In Figure 7, the system PE is plotted versus temperature for a 50Å gold nanoparticle coated with increasing densities of the alkanethiolate SAM. For the bare nanoparticle there is a discontinuity around 980K, which corresponds to a phase change. The SAM coated nanoparticle demonstrates a very different behavior. Initially, for small numbers of adsorbed alkanethiolate chains, the melting temperature of the gold nanoparticle decreases, and does not occur at a unique temperature but rather over a range of temperatures. This behavior is

expected for a mixture of two materials. The appearance of the SAM on the particle surface decreases the surface tension and internal pressure. As the coverage percentage is increased further, another behavior is observed. At higher surface coverage, above 70%, the PE of the system begins to decrease as the temperature is increased, and then after a small temperature range the PE resumes its linear increase. This behavior is explained by the mixing that occurs between the alkanethiolate chains and the gold atoms. The mixing of the SAM chains with the gold atoms is possible because of the lower binding energy of surface Au atoms. The lower binding energy means that the surface atoms will become mobile at a lower temperature than the interior gold atoms. These surface atoms begin to mix with the alkanethiol chains, and as the chains penetrate deeper into the nanoparticle they are able to interact with an ever increasing number of gold atoms. Once complete mixing has occurred, the PE resumes increasing monotonically.

Figure 7. Potential energy versus temperature for the alkanethiolate SAM coated gold nanoparticle with various amount of surface coverage

As we found in the internal pressure in Figure 5, the structure of the SAM coated gold nanoparticle is metastable. The increase of both the surface coverage and the temperature, aids this particle in transforming into a mixed structure, as shown in Figure 8. This result has not been previously predicted as it was previously assumed, that the SAM chains would desorb at these temperatures, as occurs on flat surfaces.
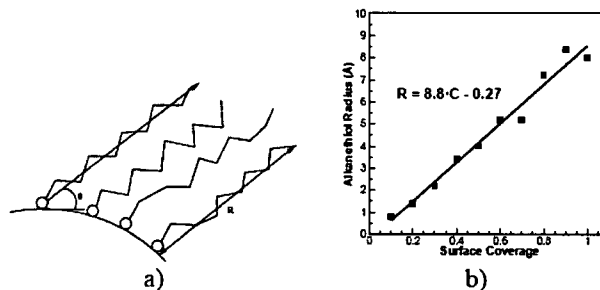
Figure 8. Cross section of 100% coated gold nanoparticle at 300K (a) and 600K (b), showing the dissolution of the alkanethiol chains at high temperatures and high 184 kJ/mol sulfur-gold binding energy

Figure 9. Difference in radial position for the head and tail groups of the alkanethiolate chains at various surface coverage densities, drawing (a) and data (b)

3.5. SAM Phases

Determining the phase diagram of the SAM chains on a gold surface is of fundamental interest. There has been extensive effort to understand the various phases of the alkanethiolate SAM chain on flat gold surfaces[37], which have found four distinct phases. In this work, as in previous work involving flat surfaces, we have investigated surface coverage and temperature as determining factors for the phase of the SAM.

One should expect that the binding energy of an alkanethiolate chain to the gold surface is dependent on whether the chain is lying along the surface of the nanoparticle (physisorption for longer chains, or chemisorption for shorter chains) or standing radially outward with only the head group sulfur atom interacting with the gold surface (chemisorption)[38].

In Figure 9, the difference in radial position of the sulfur head atom and the CH_3 tail particle is plotted for 10% to 100% surface coverage. At low surface coverage the alkanethiol chains lie along the surface of the nanoparticle as indicated by the small difference in radial positions between the CH_3 tail and the sulfur head group. In between the high and low surface coverage regions the alkanethiolate chains begin to stand radially outward from the nanoparticle surface. Above 90% surface coverage the chains have all orientated themselves with the minimally computed tilt angle from the nanoparticle surface, and the maximum difference in radial position is observed.

4. Conclusions

The alkanthiolate SAM-coated gold nanoparticle has been shown to be mechanically and chemically metastable through extensive modeling and simulation. The SAM that is adsorbed onto the surface begins to mix with the surface gold atoms at low temperatures because of the weaker gold-gold bonding of the surface atoms to the interior gold atoms. This process is more pronounced as the density of the SAM is increased, as demonstrated by the corrugation number computed previously. For full surface coverage, the SAM chains will begin to diffuse into the gold core as the temperature rises from 300K to 500K. This mixing process lowers the PE of the system. The diffusion activation energy of the sulfur atoms is measured to be low in this temperature range. Once the temperature has increased to around 600K, the alkanethiolate chains are completely mixed with the gold atoms, and the activation energy for diffusion greatly increases. The PE and diffusivity results concur with the observation that a phase change in the SAM-coated gold nanoparticle system occurs around 500K. We have therefore concluded that the melting temperature of the gold is lowered by the adsorption of alkanethiolate SAMs on the nanoparticle surface and creates a metastable system for fully covered nanoparticles of diameters around 50Å. The measured decrease in melting temperature of the nanoparticle is more pronounced as more SAM chains are adsorbed onto the nanoparticle surface. The affect of the chosen gold-gold and gold-sulfur interaction potentials has been discussed in each result section and shown to only affect the computed result quantitatively rather than qualitatively.

Acknowledgements

References

1. Manna, A., T. Imae, K. Aoi, and M. Okazaki, "Gold Nanoparticles Self-confined by Hybrid Self–Assembled Monolayers of Dendrimer and Dodecanethiol. *Molecular Simulation.*" 29(10–11), pp. 661–665, 2003.

2. Hong, R., G. Han, J.M. Fernández, B.-J. Kim, N.S. Forbes, and V.M. Rotello, "Glutathione–Mediated Delivery and Release Using Monolayer Protected Nanoparticle Carriers" *Journal of the American Chemical Society*, 128, pp. 1078–1079, 2006.

3. Magnusson, M.H., K. Duppert, J.-O. Malm, J.-O. Bovin, and L. Samuelson, "Size–Selected Gold Nanoparticles by Aerosol Technology." *NanoStructured Materials*, 12, pp. 45–48, 1999.

4. Chiang, C.-L., "Controlled Growth of Gold Nanoparticles in Aerosol–OT/Sorbitan Monooleate/Isooctane Mixed Reverse Micelles. *Journal of Colloid and Interface Science*, 230:60–66, 2000.

5. J.-U. Kim, S.-H. Cha, K. Shin, J. Y. Jho, and J.-C. Lee. Synthesis of Gold Nanoparticles from Gold(I)-Alkanethiolate Complexes with Supramolecular Structures through Electron Beam Irradiation in TEM." *Journal of the American Chemical Society Communications*, 127, pp. 9962–9963, 2005.

6. Nuzzo, R.G., B.R. Zegarski, and L.H. Dubois, "Fundamental Studies of the Chemisorption of Organosulfur Compounds on Au(111). Implications for Molecular Self-Assembly on Gold Surfaces." *Journal of the Americal Chemical Society*, 109, pp. 733–740, 1987.

7. Strong, L. and G.M. Whitesides, "Structures of Self–Assembled Monolayer Films of Organosulfur Compounds Adsorbed on Gold Single Crystals: Electron Diffraction Studies." *Langmuir*, 4, pp. 546–558, 1988.

8. Rosenbaum, A.W, M.A. Freedman, S.B. Darling, I. Popova, and S.J. Sibener, "Surface Vibrations in Alkanethiol Self-Assembled Monolayers of Varying Chain Length." *Journal of Chemical Physics*, 120(8), pp. 3880–3886, 2004.

9. Luetke, W.D., U. Landman, "Structure, Dynamics, and Thermodynamics of Passivated Gold Nanocrystallites and Their Assemblies." *The Journal of Physical Chemistry*, 100(32), pp. 13323–13329, 1996.

10. Bhatia, R. and B.J. Garrison, "Phase Transitions in a Methyl–Terminated Monolayer Self-Assembled on Au{111}." *Langmuir*, 13, pp. 765–769, 1997.

11. Masens, C., M.J. Ford, and M.B. Cortie, "The Effect of Surface Symmetry on the Adsorption Energetics of SCH₃ on Gold Surfaces Studied Using Density Functional Theory." *Surface Science*, 580, pp. 19–29, 2005.

12. Landman, U. and W. D. Luedtke. "Small is different: energetic, structural, thermal, and mechanical properties of passivated nanocluster assemblies." *Faraday Discussions* 125, pp. 1–22, 2004.

13. Daw, M.S. and M.I. Baskes, "Embedded–atom method: Derivation and application to impurities, surfaces, and other defects in metals." *Physical Review B*, 29(12), pp. 6443–6453, 1984.

14. Foiles, S.M., M.I. Baskes, and M.S. Daw, "Embedded–atom–method functions for the fcc metals Cu, Ag, Au, Ni, Pd, Pt, and their alloys." *Physical Review B*, 33(12), pp. 7983–7991,

1986.

15. Pu, Q., Y. Leng, L. Tsetseris, H.S. Park, S.T. Pantelides, and P.T. Cummings, "Molecular dynamics simulations of stretched gold nanowires: The relative utility of different semiempirical potentials." *The Journal of Chemical Physics*, 126, pp. 144707, 2007.

16. Mei, J., J.W. Davenport, and G.W. Fernando, "Analytic embedded–atom potentials for fcc metals: Application to liquid and solid copper." *Physical Review B*, 43(6), pp. 4653–4658, 1991.

17. Stave .M.S., D.E. Sanders, T.J. Raeker, and A.E. DePristo, "Corrected effective medium method. V. Simplifications for molecular dynamics and Monte Carlo simulations." *Journal of Chemical Physics*, 93(6), pp. 4413–4426, 1990.

18. Raeker, T.J and A.E. DePristo, "Theory of chemical bonding based on the atom–homogeneous electron gas system." *International Reviews in Physical Chemistry*, 10(1), pp. 1–54, 1991.

19. Lee, B. and K. Cho, "Extended embedded–atom method for platinum nanoparticles." *Surface Science*, 600, pp. 1982–1990, 2006.

20. M. I. Haftel. Surface Reconstruction of Platinum and Gold and the Embedded–Atom Method. *Physical Review B*, 48(4), pp. 2611–2622, 1993.

21. Plimpton, S.J., "Fast Parallel Algorithms for Short–Range Molecular Dynamics." *Journal of Computational Physics*, 117, pp. 1–19, 1995.

22. Andersen, H.C, "RATTLE:. A Velocity Version of the SHAKE Algorithm for Molecular Dynamics." *Journal of Computational Physics*, 52, pp. 24–34, 1983.

23. Shevade, A. V., J. Zhou, M. T. Zin, and S. Jiang. Phase Behaviour of Mixed Self-Assembled Monolayers of Alkanethiols on Au(111): A Configurational-Bias Monte Carlo Simulation Study. *Langmuir* 17, pp. 7566–7572, 2001.

24. Rai, B., P. Sathish, C.P. Malhotra, Pradip, and K.G. Ayappa, "Molecular Dynamic Simulations of Self-Assembled Alkylthiolate Monolayers on an Au(111) Surface." *Langmuir*, 20, pp. 3138–3144, 2004.

25. Beardmore, K.M., J.D. Kress, N. Gronbech-Jensen, and A.R. Bishop, "Determination of the headgroupgold(111) potential surface for alkanethiol self-assembled monolayers by ab initio calculation." *Chemical Physics Letters*, 286, pp. 40–45, 1998.

26. Mahaffy, R., R. Bhatia, and B.J. Garrison, "Diffusion of a Butanethiolate Molecule on a Au(111) Surface." *Journal of Physical Chemistry B*, 101, pp. 771–773, 1997.

27. Zhang, L., W.A. Goddard III, and S. Jiang, "Molecular simulation study of the c(4x2) superlattice structure of alkanethiol self-assembled monolayers on Au(111)." *Computers in Chemical Engineering*, 22(10), pp. 1381–1385, 2002.

28. Lavrich, D.J., S.M. Wetterer, S.L. Bernasek, and G. Scoles, "Physisorption and Chemisorption of Alkanethiols and Alkyl Sulfides on Au(111). "*Journal of Physical Chemistry B*, 102, pp. 3456–3465, 1998.

29. Jang, S.S.,Y.H. Jang, Y.-H. Kim, W.A. Goddard III, A.H. Flood, B.W. Laursen, H.-R. Tseng, J.F. Stoddart, J.O. Jeppesen, J.W. Choi, D.W. Steuerman, E. Delonno, and J.R. Heath, "Structures and Properties of Self-Assembled Monolayers of

Bistable [2]Rotaxanes on Au(111) Surfaces from Molecular Dynamics Simulations Validated with Experiment." *Journal of the American Chemical Society*, 127, pp. 1563–1575, 2005.

30. Lewis, L J., P. Jensen, J.-L. Barrat," Melting, Freezing, and Coalescence of Gold Nanoclusters." *Physical Review B*, 56(4), pp. 2248–2257, 1997.

31. Badia, A,. L. Cuccia, L. Demers, F. Morin, and R.B. Lennox, "Structure and Dynamics in Alkanethiolate Monolayers Self-Assembled on Gold Nanoparticles: A DSC, FT–IR, and Deuterium NMR Study." *Journal of the Americal Chemical Society*, 119, pp. 2682–2692, 1997.

32. Thompson, S.M., K.E. Gubbins, J.P. R.B. Walton, R.A.R. Chantry, and J.S. Rowlinson, "A molecular dynamics study of liquid drops." *Journal of Chemical Physics*, 81(1), pp. 530–542, 1984.

33. Winn, J.S., *Physical Chemistry*, Addison Wesley, Boston, MA, 1995.

34. Lang, G., *Handbook of Chemistry and Physics, 55th edition*, CRC Press, Cleveland, OH, 1974.

35. Hawa, T. and M.R. Zachariah, "Coalescence Kinetics of Bare and Hydrogen-Coated Silicon Nanoparticles: A Molecular Dynamics Study." *Physical Review B*, 71, pp. 165434, 2005.

36. Dieter, G.E., *Mechanical Metallurgy*, McGraw-Hillm Inc., New York, NY, 1986.

37. Schreiber, F., "Self-assembled monolayers: from 'simple' model systems to biofunctionalized interfaces." *Journal of Physic: Condensed Matter*, 16, pp. R881–R900, 2004.

38. Lavrish, D.J., S.M. Wetterer, S.L. Bernasek, and G. Scoles, "Physisorption and Chemisorption of Alkanethiols and Alkyl Sulfides on Au(111)." *Journal of Physical Chemistry B*, (102), pp. 3456–3465, 1998.